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Diffuse Reflectance Fourier Transform Infrared Spectroscopic Study of
Chemical Bonding and Hydrothermal Stability
of an Amino Silane on Metal Oxide Surfaces

by

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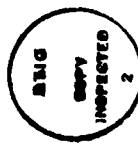
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INTRODUCTION

The surface composition of glasses and the surface treatment can affect the performance of the fiber reinforced plastics. Heat treatment, additives, etching, and surface leaching are often used in the commercial production process to improve the durability, hardness, chemical resistance and adhesion. The chemical analysis of the surface is essential to understand the nature of these effects.

Various techniques were employed in order to obtain the chemical analysis of the surface. Difficulties often arise due to the sensitivity of the technique. The isolation of the surface property from the bulk property has proven to be tedious or difficult in many cases. The characterization of glass/epoxy and glass/silane interfaces was reported by using ion scattering spectroscopy (ISS) and secondary ion mass spectroscopy (SIMS) [1]. When the ion sputtering technique was used on an incompletely cured silane coating, the SIMS spectra at different depths of penetration revealed that, within a region of 250Å of the glass silane interface, three interphase domains exist. Auger Electron Spectroscopy (AES), a surface technique, was used to obtain the composition of glass [2]. This technique was used to depth profile the first 10 - 50Å of the surface. In order to understand the nature of the chemical interaction on the surface of glass, it is necessary to use techniques which can yield information about molecular structure. Shih and Koenig [3] showed that the Raman spectroscopy could be used to characterize silane coupling agents in the bulk, in aqueous solution and on glass fiber surfaces. When a coupling agent was applied to glass fibers from aqueous solution, polyvinylsiloxane polymer was found by Raman spectroscopy to be

chemically bonded to the glass surface (4). Chiang et al. [5] used solid state ^{13}C NMR to characterize the structure of a silane coupling agent on glass fiber surface. X-ray photoelectron spectroscopy was used by Moses et al. [6] to observe the reactions of alkylamine-silane with metal oxide electrode. Several bonding schemes were found to be possible on metal oxide surfaces.

Infrared spectroscopy is widely used to study the molecular structure and chemical composition of surfaces [7,8]. The classical infrared transmission method provides both qualitative and quantitative information on the surface species [9] and has been extensively employed. With the development of Fourier transform infrared spectroscopy (FT-IR) and improvement of the signal-to-noise ratio, several methods of infrared spectroscopy were successfully employed to obtain spectra. The reflection-absorption technique showed that the molecular structure of silane treated on metal substrates could be obtained [10]. Recent work by Yoshida et al. [11] typifies that the reflection-absorption technique can also provide information on molecular orientation of surface species on metal substrates. The attenuated total reflection (ATR) technique has been used to study the silane layers [12]. Crystalline Al_2O_3 was used as a substrate. The extent of hydrolysis and cross-linking of silane layers were studied by this technique.

The diffuse reflectance technique was developed many years ago [13,14]. The diffusely reflected light is collected by a mirror and transmitted to the detector (see fig. 1). The basic principles of this technique were developed by Kubelka-Munk [13]. The sample is placed in a sample pan and the spectrum is ratioed with a pure KBr spectrum. The unit of absorption is the Kubelka-Munk unit which has the relationship as shown below:

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty}$$

[1]

where R_∞ is the absolute reflectance of the layer.

The spectral information depends on the particle size and the scattering coefficient. Qualitative information can easily be obtained. However, quantitative information is ambiguous at high concentrations [15]. To perform an accurate spectral subtraction, Kubelka-Munk units of components to be subtracted must be low [16]. The sample may be diluted with KCl or KBr powder. Some of the advantages in using the diffuse reflectance technique are that it requires no sample preparation so the unperturbed structure of the molecules adsorbed on the surface can be studied. The conventional sample preparation method where KBr powder is ground with the sample and pressed into a pellet is completely avoided in the diffuse reflectance technique. In the diffuse reflectance method, a sample can be examined directly with or without dilution with KBr powder.

In fiber reinforced plastic technology, glass fibers or other types of fillers are used as reinforcements or as extenders to the material. The essence of understanding molecular bonding at the surface of glass fibers or fillers is indispensable for the improved technology. Since glass fibers are composed of various metal oxides, it is essential to elucidate the role of these metal oxides on the structure of the silanes. With different types of oxides present in glass fibers, the aminosilane can react differently toward these metal oxides. Each oxide has its own intrinsic characteristics such as surface isoelectric point [17]. Aminosilanes have been used in fiber reinforced plastic technology. Extensive research on its molecular structure reveals that this compound can form many structures depending on the pH of the treating solution and also the drying conditions [18]. Hence, the structure of aminosilanes may especially be vulnerable to the microheterogeneity

of the surface. The key to good mechanical performance and efficient processing of composite systems lie in the properties of the filler/resin interface. The physical and chemical states of the filler surface strongly affect the nature, type, concentration, orientation, and the distribution of silane on the surface.

When silane is applied on the surface, silane can chemisorb, physisorb and cross polymerize. The metal-oxide-silane (M-O-Si) bond is believed to be partly responsible for the coupling stability.

In this paper we will characterize the surface of treated metal oxides by using transmission and diffuse reflectance Fourier transform infrared spectroscopy. Immersion test will show what type of surface will be more hydrolytically stable in hot water. The results will provide a mechanistic understanding of how the surface of reinforcements and an aminosilane interact. In order to obtain information about the hydrothermal stability of the interfacial bonds, we have chosen monoalkoxy silane.

EXPERIMENTAL

Aluminum oxide, titanium oxide, and silica powders with a specific surface area of 130, 100, and 50 m^2/g respectively, were kindly supplied by Mr. Lierson of Degussa, Inc. γ-aminopropyldimethylethoxysilane (γ-APDMES) was purchased from Petrarch System Inc. and used as received. One percent and a 0.2% by weight of γ-APDMES was hydrolyzed in deionized distilled water for 40 minutes. Metal oxide powder was immersed in the solution for 15 minutes. The retrieval of the powder was made by centrifuging and the solution was decanted. The treated powder was dried in air at room temperature for one day and heated in 80°C for one day. Immersion test was made by placing the treated powder in 80°C distilled water. The powder was retrieved from the water at various intervals for infrared analysis.

The amount of γ-APDMES was calibrated by transmission infrared technique. γ-APDMES was allowed to hydrolyze by absorbing moisture from air for three weeks. The surface of the sample was scratched on several occasions to ensure complete exposure to moist air. The dried sample was carefully weighed with a Perkin Elmer microbalance with the accuracy of ±0.0001 mg. The weighed sample was ground with KBr powder and compressed into a pellet for infrared analysis.

A Fourier transform infrared spectrometer (Digilab FTS-20E) was used to obtain the spectral information. The spectrometer was constantly purged with dry nitrogen. A nitrogen cooled Mercury Cadmium Telluride (MCT) detector was used for high sensitivity data collection. A Digilab DRA-100 diffuse reflectance accessory with hemispherical mirrors was placed in the sample chamber and used to collect the diffusely scattered light from the sample. To improve the signal-to-noise ratio, long scanning period of 600 scans was utilized at resolution 4 cm^{-1}, but in many instances 200 scans was sufficient.

The calibrations of powders were done by carefully weighing the powder with a microbalance. The weighed powders were ground with approximately 200 mg of KBr powder and pressed into a pellet. The transmission infrared technique was used to monitor the intensity of the intrinsic peaks due to the powders versus the weight in milligrams of the powders.

Isopropyltriisostearoyltitanate (KR-TTS) and di(dioctylpyrophosphato) ethylene+methacrylic functional amine (KR-238M) (kindly supplied by Mr. S. Monte, Kenrich Petroleum Inc.) were used to treat silica. The coupling agent solution was prepared from 0.5% by weight of ethanol. The powder was mixed in the solution for 30 minutes. After centrifuging, the excess ethanol was decanted and the powder was dried in vacuum at room temperature. The samples were examined by diffuse reflectance infrared technique.

Preparation of sample for the diffuse reflectance spectroscopy requires only diluting the sample with KBr powder. No grinding was applied during the preparation. The single beam spectrum of the sample was ratioed with a single beam spectrum of pure KBr powder. Through mathematical manipulation, the spectrum has a Kubelka-Munk unit.

RESULTS

Figure 2 shows the diffuse reflectance spectra of silicon oxide, titanium oxide, and aluminum oxide powders. The choice of these powders in this experiment is justified by the fact that silica is a major component in glass fibers. Titania and alumina powders were used since the isoelectric point of these powders is different from silica and covers a wide pH range. Therefore, the surface charge effect may be observed. Another reason for choosing titanium and aluminum oxide powders is the nature of the infrared absorption of these powders. From fig. 2B and 2C, it can be seen that these two powders do not absorb in the region of interest where the silane coupling agent absorbs the infrared. Aminosilane coupling agent has major absorption bands from 1600 to 900 cm^{-1}. The region around 1600 cm^{-1} yields information concerning the amine group. The band around 1000 cm^{-1} is informative about the siloxane bond and perhaps the metal-O-Si bond. The peak at 3750 cm^{-1} in fig. 2 is due to the free surface silanol of silica powder [19]. The band at 1080 cm^{-1} is due to the Si-O-Si stretching mode of silica. This region overlaps with the Si-O-Si stretching mode of the silane coupling agent itself. Titanium oxide (fig. 2B) has a strong band at 700 cm^{-1} whereas aluminum oxide (fig. 2C) has a strong absorbance at 830 cm^{-1}.

Figure 3C shows the difference spectrum of the treated silica powder (fig. 3A) minus the untreated powder (fig. 3B). The difference spectrum

reveals the information of the surface treatment and the possible chemical changes that may occur. From the difference spectrum (fig. 3C), the peak at 1596 cm^{-1} is assigned to the NH$_2$ deformation mode of the silane coupling agent molecule. A weak band at 1412 cm^{-1} and a strong band at 1257 cm^{-1} are due to the antisymmetric and symmetric deformation modes of the SiCH$_3$ group, respectively.

Figure 4A is the spectrum of titanium oxide treated with γ-APDMES from cyclohexane. Figure 4C is the difference spectrum of the treated titanium oxide minus the untreated sample. The NH$_2$ band is noticeable. The location of the NH$_2$ deformation band of the treated titanium oxide sample shifted downward from 1596 cm^{-1}, in the case of silica, to 1584 cm^{-1}. The intensity of this band is also enhanced when compared with the neat γ-APDMES spectrum (fig. 5) and the difference spectrum of γ-APDMES treated on silica (fig. 3C).

Figure 6 shows the spectrum of n-propylamine on titanium. The amine band shifts from 1600 cm^{-1} of the neat sample to 1575 cm^{-1} when it is on titanium oxide surface. The enhanced intensity at 1575 cm^{-1} band is also noticeable. After the sample was evacuated at room temperature for 12 hours, n-propylamine still remains on the surface of titanium oxide. It is likely that amine interacts with titanium oxide via hydrogen bonding and perhaps complexing with titanium atom which results in enhanced intensity.

The band at 1058 cm^{-1} is assigned to the Si-O-Si antisymmetric stretching mode [20,21]. The presence of this band indicates that coupling agent dimers are present on the surface. The absorbance ratio of the 1058 cm^{-1} to 1275 cm^{-1} bands of the hydrolyzate is 1.2 whereas the absorbance ratio of these two bands of γ-APDMES on the surface is 0.8. The relative intensity of this dimer peak (1058 cm^{-1}) with the SiCH$_3$ peak (1257 cm^{-1}) is comparatively low compared to the spectrum of the condensed dimers of the hydrolyzate of γ-APDMES

since the SiCH$_3$ group exists regardless of the interfacial reaction. Another peak is observed at 950 cm^{-1}. With the presence of this 950 cm^{-1} band, the low intensity of the dimer peak at 1058 cm^{-1} is justified. Some γ-APDMES molecules may condense and form dimers while some of the remaining molecules may form a chemical bond to the titanium oxide surface. With the presence of 950 cm^{-1} band and the lower intensity of the dimer peak at 1058 cm^{-1}, the band at 950 cm^{-1} is tentatively assigned to the surface bonding of titania and silane coupling agent (Ti-O-Si).

To support the assignment of 950 cm^{-1} band, titanate coupling agents (KR-TTS and KR-238M) were treated on the surface of silica powder with a specific area of 380 m^2/gm. Figures 8 and 9 show the spectra of neat titanate coupling agents. When the untreated silica (fig. 10B) is subtracted from the titanate treated sample (fig. 10A), the difference spectrum (fig. 10C) reveals an appearance of a peak at 950 cm^{-1}. The difference spectrum (fig. 11C) of silica treated with KR-238M also reveals a band at 950 cm^{-1}. This evidence supports the assignment of the 950 cm^{-1} band which may be due to Ti-O-Si.

Figures 12A and 12B are the spectra of γ-APDMES treated and distilled water-wetted samples of aluminum oxides, respectively. The difference spectrum of treated aluminum powder (fig. 12C) shows a peak at 1575 cm^{-1}. This peak can be assigned to the NH$_2$ deformation mode. The frequency of this peak is now at 1575 cm^{-1} as compared to 1596 cm^{-1} for silica and 1584 cm^{-1} for titania samples. A band at 1058 cm^{-1} which was assigned to the Si-O-Si stretching mode of silane is present along with a new band at 963 cm^{-1}. Again the absorbance ratio of SiCH$_3$ at 1275 cm^{-1} to the dimer (Si-O-Si) peak at 1058 cm^{-1} is lower (0.7) when compared to the absorbance ratio of condensed dimer of the γ-APDMES hydrolyzate (1.2) The same argument can be used to explain the

appearance of 963 cm^{-1} band. The presence of 963 cm^{-1} band and the lower intensity of 1058 cm^{-1} band lead to the tentative assignment of the 963 cm^{-1} band to be due to the surface reaction of silane and aluminum oxide surface (Al-O-Si).

In order to investigate the hydrothermal stability of γ-APDMES on oxide surfaces, the powders treated with 1% γ-APDMES by weight were immersed in distilled water at 80°C. It was observed that the aluminum oxide sample sank immediately in the hot water, whereas slight difficulty was experienced with the titanium oxide powder and required more than 20 minutes before immersion. The treated silicon oxide, however, did not immerse even when vigorous agitation was applied. Figure 13 shows the infrared transmission spectra of untreated aluminum oxide (fig. 13A) and the treated (fig. 13B) samples. The small peak at 1257 cm^{-1} due to the SiCH$_3$ groups is used as an indication of the amount of silane remaining on the surface of the powder after immersion in 80°C water. The peak at 830 cm^{-1} is used as the internal thickness band. Figure 14 shows the spectra of titanium oxide treated with γ-APDMES immersed in 80°C water as a function of immersion time. Figure 15 is the calibration curve of γ-APDMES. The area of the peak at 1257 cm^{-1} is plotted versus the weight of γ-APDMES. Figure 16 is the calibration curves for silica, aluminum oxide and titanium oxide powders. The absorbances at 1058, 830, and 690 cm^{-1} of silica, aluminum oxide, and titanium oxide were plotted against the weight of the powders. With the calibration curves of γ-APDMES and powder, the amount of γ-APDMES present per milligram of oxide powder can be plotted versus immersion time as shown in fig. 17. It can be seen that silane treated on aluminum oxide powder desorbs at a much faster rate than on the titanium oxide sample.

The stability of the interfacial bond between silane and metal oxide surface is an important factor in the hydrothermal stability of composite materials. Water can hydrolyze the oxane bond and sever the interfacial linkage. In order to study the hydrothermal stability of the silane at low coverages, metal oxide powders were treated with 0.2% by weight of γ-APDMES. The amount of silane coupling agent adsorbed on the powder surface of the sample before immersion test was calculated by using the transmission infrared technique. The same sample was also examined by using the diffuse reflectance infrared technique. The samples that were retrieved from the immersion test were all examined by the diffuse reflectance technique. The amount of silane present on the powder surface can be calculated by relating the diffuse reflectance spectrum with the transmission spectrum of the sample before the immersion test.

The treated powders were immersed in 80°C distilled water. All three powders immersed easily in the water, unlike the previous case where silica treated with 1% γ-APDMES did not immerse. The powders were recovered at various intervals for infrared examination. The curves in fig. 18 show the comparison of the desorption of γ-APDMES from three different powders. It can be seen that aluminum oxide loses silane molecules at the fastest rate, whereas silica maintains silane molecules the longest.

The desorption of n-propylamine treated on titanium oxide was also examined. Figure 19 shows the spectra of the sample retrieved after various immersion time in 80°C water. By examining the CH band around 2930 cm^{-1} due to the propyl chain, it can be observed that n-propylamine desorbs almost completely within ten minutes of immersion time. The rapid desorption of n-propylamine may be due to the absence of chemical bonding on titanium oxide

surface. It further indicates that coordination and/or hydrogen bonding of amine play a little role in desorption resistance.

It was also observed that γ-APDMES does not adsorb very strongly onto the aluminum oxide surface when compared with titanium oxide or silica. The low amount of adsorption may be influenced by the surface isoelectric point (IEP) of aluminum oxide which is 9.1. The surface of aluminum oxide in silane solution is near neutral and there is no strong interaction of silane to the aluminum oxide surface. However, silica, which has IEP ≈ 2.2, is more negatively charged in the silane solution. Strong interaction of amine group of the silane molecule may exist with silica. Therefore, a higher adsorption of silica is observed with silica samples.

DISCUSSION

The appearance of the peak at 963 cm^{-1} in the difference spectrum of silane treated aluminum was tentatively assigned to the Al-O-Si stretching mode. The frequency of Al-O-Si stretching mode can be calculated by a simple harmonic oscillator model where the nuclei represent a point mass and the bonding force between nuclei represents a spring constant according to Hook's law [20]. For an oscillator $M_1-M_2-M_1$ where M_1 and M_2 represent unequal masses, in this case two different atoms, antisymmetric stretching frequency, ν, in cm^{-1} can be represented by [20]:

$$\nu = 1303 \sqrt{F\left(\frac{1}{m_1}+\frac{2}{m_2}\right)} \qquad [2]$$

where F is the force constant in dynes/cm, and m_1 and m_2 are the masses in grams. From the spectra of pure oxide, the frequency of $M_1-M_2-M_1$ is known. Therefore the force constant can be calculated from equation 2.

For linear M_1-M_2-M_3 model, the stretching frequencies can be derived by the following equation:

$$\nu = 1303\sqrt{\lambda} \qquad [3]$$

where λ can be obtained by solving the following quadratic equation:

$$\lambda^2 - \lambda[F_1(\frac{1}{m_1}+\frac{1}{m_2}) + F_3(\frac{1}{m_2}+\frac{1}{m_3})] + F_1F_3(\frac{1}{m_1m_2}+\frac{1}{m_2m_3}+\frac{1}{m_1m_3}) = 0 \qquad [4]$$

where F_1 is the force constant between atom 1 and atom 2.

F_3 is the force constant between atom 2 and atom 3. Given the masses of each atom and the force constants which are obtained from equation 2, λ is calculated from equation 4 and substituted in equation 3 to yield the frequency.

Since the frequencies of Si-O-Si and Al-O-Al are known to be 1058 and 830 cm^{-1}, the force constants F_1 and F_3 are calculated from equation 2 to be 2.50 and 4.11 mdynes/Å respectively. For Al-O-Si bond, λ is calculated from equation 4 by substituting $M_1 = 26.98$, $M_2 = 16.00$, $M_3 = 28.09$, $F_1 = 2.50$, and $F_3 = 4.11$. The two results from quadratic equation yield $\lambda = 0.54$ and 0.11. Substituting λ into equation 3, the two frequencies are 958 and 434 cm^{-1}, which correspond to antisymmetric and symmetric stretching frequencies, respectively.

The calculated frequency of Al-O-Si at 958 cm^{-1} agrees well with that observed in fig. 11C. When digital subtraction was performed, the reference (untreated) sample was first wetted with distilled water and dried. The reason for doing so is to eliminate the difference due to dry and wet samples as well as the possible artifact. It was observed that dry and wet-then-dry of untreated silane samples are different. When these two untreated samples were subtracted, a peak around 960 cm^{-1} appeared along with the water peak at 1640 cm^{-1}. Hence, a great caution must be taken to interpret the band in this frequency range.

Ishida et al. [21] showed that the SiCH$_3$ band at 1255 cm^{-1} had a slightly lower intensity than the dimer (Si-O-Si) peak at 1058 cm^{-1} of the hydrolyzate of γ-APDMES. With the observation of the lowering in intensity of dimer peak at 1058 cm^{-1} compared with SiCH$_3$ peak at 1258 cm^{-1} plus an appearance of 963 cm^{-1} band, the band at 963 cm^{-1} is tentatively assigned to the Al-O-Si inter-facial bond. The peak at 963 cm^{-1} can therefore be assigned to the Al-O-Si antisymmetric stretching mode. This evidence indicates that silane coupling agent forms a chemical bond on the aluminum oxide surface.

When the sample is rinsed with THF, the dimers which are not chemically bonded to the surface can be washed away. The reduction in intensity of 1058 cm^{-1} peak is the consequence of the dimer desorption. It was noted that not all dimers desorb upon THF wash, probably due to the amine groups that are interacting directly with the surface.

The same calculation procedure was made with Ti-O-Si bond. The force constant of Ti-O-Ti stretching was found to be 1.92 mdynes/Å. With the known masses and force constants, λ's were calculated from equation 4 to be 0.50 and 0.07. Substituting λ into equation 3, the stretching frequencies were determined to be 921 and 344 cm^{-1}. In fig. 4C, a band at 950 cm^{-1} is observed and is assigned to the Ti-O-Si bond. With the experiment done with titanate coupling agents on silica, an appearance of a 950 cm^{-1} band obtained after spectral subtraction of untreated sample from treated sample supports the assignment of Ti-O-Si bond to be 950 cm^{-1}. The precise frequence agreement may be accidental coincidence.

The surface charge may have an influence on the orientation of the silane molecule adsorbed on the surface. The degree of surface charge can be determined by the isoelectric point (IEP). IEP is determined by the pH at which the

surface will be neutral. Silica, titanium oxide, and aluminum oxide have IEP of 2.2, 6.0, and 9.1 respectively [17]. A cationic silane such as γ-APDMES can have an interaction with the surface through the amine group at the end of the propyl chain. In the difference spectra of treated powders, the positions of an amine deformation are different. Spectrum of treated aluminum oxide powder (fig. 12C) shows a peak at 1575 cm^{-1} along with an enhanced intensity. The enhanced intentisy indicates that the amine group interacts with the surface. It should be noted that an un-heat treated sample usually shows the amine deformation band at 1575 cm^{-1} due to the aminebicarbonate salt. Since the sample has been heat treated and the characteristic bicarbonate band at 1330 cm^{-1} is absent, the aminebicarbonate salt is out of consideration. Illustrated in fig. 4C is the amine deformation frequency of treated titanium oxide sample at 1584 cm^{-1}. The enhanced intensity of the amine deformation band is also observed as in the case of treated alumina sample. Spectroscopic evidence indicates that the conformation of the silane molecule is different on different metal oxide surfaces.

Due to the surface hererogeneity, the possibility of amine coordinating with metal atom cannot be excluded. The enhancement in intensity of amine band around 1600 cm^{-1} indicates that amine interacts with the surface. Complexation of amine to metal such as titanium atom was found possible [22]. When n-propylamine was treated on titanium oxide, an enhanced intensity of amine deformation band was also observed. When the sample was evacuated for 12 hours at room temperature, n-propylamine could not be removed from the surface. It can be concluded that amine interacts with the surface and also influences the adsorption characteristics.

Immersion test shows that desorption of silane is more rapid in the case of aluminum oxide powder than titanium oxide powder. The treated silica, on

the other hand, maintains the coupling agent the longest period during the immersion test. Two major causes can be considered. First, the hydrophilicity of the treated aluminum oxide surface helps water to interact quickly with the silane. However, the equilibrium of water penetration into the silane layers may be reached quickly since the thickness of the silane is at most a few layers. Second, the hydrothermal stability of various Si-O-M bond may be different. For the practical application in FRP industry, the composition of glass fibers may be important in designing hydrothermally stable materials. The contribution of different amounts of metal oxide changes the IEP of the material and, therefore, can change the conformation of the silane molecules at the interface.

It is not clear as the present time whether microheterogeneity exists on the glass fiber surface. However, it is likely that the various M-O-Si bonds at the interface have different hydrothermal stability. The weaker bonds may be preferentially hydrolyzed. The hydrolyzed bonds yield hydrolysis which function as driving force for further water collection creating water pockets. The water pockets impose a strong osmotic pressure on the surrounding chains. The tensile stress in the surrounding chains reduces the hydrothermal stability due to the mechanochemical mechanism and eventually leads to cata-strophic failure of the silane layers.

CONCLUSIONS

Diffuse reflectance FT-IR spectroscopy was used to study the structure of γ-APDMES on metal oxide surfaces. It was found that the structure of silane depends on the substrate. The enhancement in intensity of amine band around 1600 cm^{-1} indicates that the amine group can coordinate with the metal surface. The silanol group of γ-APDMES can form a chemical bond with the metal oxide surface. Diffuse reflectance spectra show a peak around 963 cm^{-1}

for the interfacial Al-O-Si bond and at 950 cm^{-1} for the interfacial Ti-O-Si

bond. Immersion experiments show different hydrophobicity of the 1% silane

treated metal oxide surfaces. The treated alumina immerse easily in water

and lose the coupling agent at a faster rate during immersion test when com-

pared with treated titania and silica. The surface isoelectric point could

be an important factor in determining the orientation of the silane, especially

the silane layers in the immediate vicinity of the oxide surfaces.

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FIGURE CAPTIONS

1. Schematic diagram of the mirror setup of the diffuse reflection accessory
    unit by Digilab.

2. Diffuse reflectance infrared spectra of A) silica, B) titanium oxide, and
    C) aluminum oxide. The absence of infrared absorption in the region between
    1600 and 800 cm^{-1} of titanium and aluminum oxides facilitates the study of
    aminosilane compound.

3. Diffuse reflectance infrared spectra of A) treated silica with 1% γ-APDMES
    by weight; B) untreated silica, and C) the difference spectrum (A - B).

4. The difference spectrum (C) of treated titanium oxide (A) and untreated
    titanium oxide (B) reveals the structure of γ-APDMES adsorbed onto the
    surface.

5. FT-IR transmission spectrum of neat γ-APDMES between KBr plates.

6. Diffuse reflectance spectrum of n-propylamine adsorbed on titanium oxide.

7. Spectrum of γ-APDMES hydrolyzate. The peak at 1257 cm^{-1} is lower in inten-
    sity than the dimer (Si-O-Si) peak at 1058 cm^{-1}.

8. Spectrum of neat KR-TTS titanate coupling agent.

9. Spectrum of neat KR-238M titanate coupling agent.

10. Diffuse reflectance spectrum of A) KR-TTS treated silica; B) untreated silica;
    and C) the difference spectrum (A - B) shows a new peak at 950 cm^{-1}.

11. Diffuse reflectance spectrum of A) KR-238M treated silica; B) untreated silica;
    and C) the difference spectrum (A - B).

12. Diffuse reflectance infrared spectra of A) γ-APDMES treated aluminum oxide; B) untreated aluminum oxide; and C) the difference spectrum.

13. Transmission infrared spectrum of A) untreated aluminum oxide and B) treated aluminum oxide with γ-APDMES. The peak at 1258 cm^{-1} due to $SiCH_3$ is used as an indication of the amount of silane present on the surface.

14. Spectra of titanium oxide treated with γ-APDMES. γ-APDMES desorbs as a function immersion time.

15. Calibration curve for γ-APDMES. The area under the 1258 cm^{-1} band is plotted against the weight in milligram.

16. Calibration curves for silica, aluminum oxide, and titanium oxide powders. The absorbances at 1058, 830, and 690 cm^{-1} are plotted against the weight of the powders.

17. Desorption curve of γ-APDMES. The number of γ-APDMES molecules remaining on the powder per milligram of powder is plotted as a function of immersion time.

18. Desorption curve of γ-APDMES at low coverage on silica, titanium oxide, and aluminum oxide powders.

19. Spectra of n-propylamine treated titanium oxide as a function of immersion time in 80°C water. Most of the n-propylamine desorbs within 10 minutes.

Diffuse Reflectance
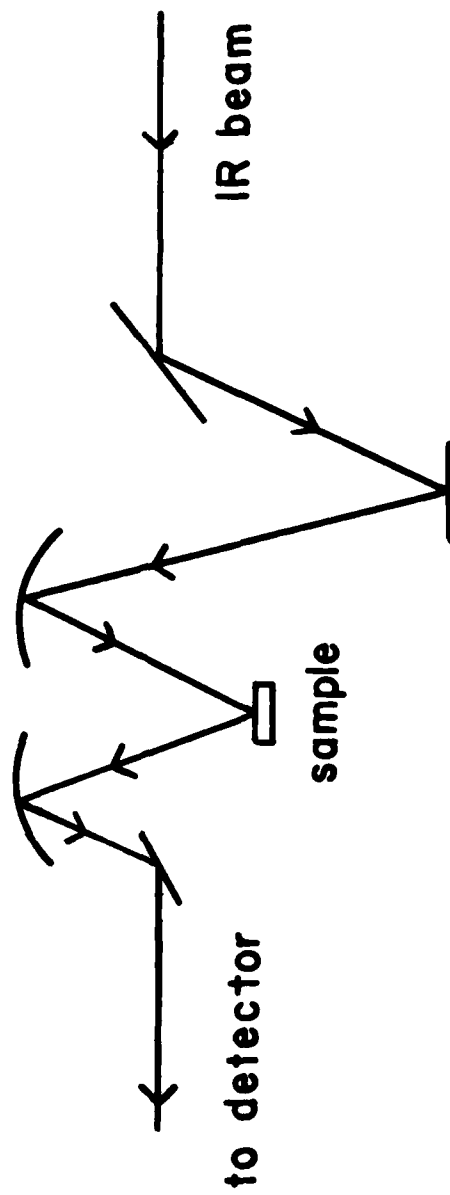
IR beam

sample

to detector

Figure 1

Figure 2

A

B

C

3500   2500   1500 cm⁻¹

Figure 3

Silica

A.

B.

C. = A – B

1596

1412

1257

1800   1600   1400   1200   800 cm⁻¹

Figure 4

TiO_2

A.

B.

C. A-B

1584

1412

1257

1058

950

1600   1200   cm^{-1} 800

Figure 5

r-APDMES

Figure 6

n-Propylamine on TiO$_2$

cm^{-1}

1000

2000

3000

Figure 7

Figure 8

KR-TTS

isopropyl, triisostearoyl titanate

3600   2800   2000   1200 cm⁻¹

Figure 9

KR-238M

di(dioctylpyrophosphato)
ethylene titanate +
methacrylic functional amine
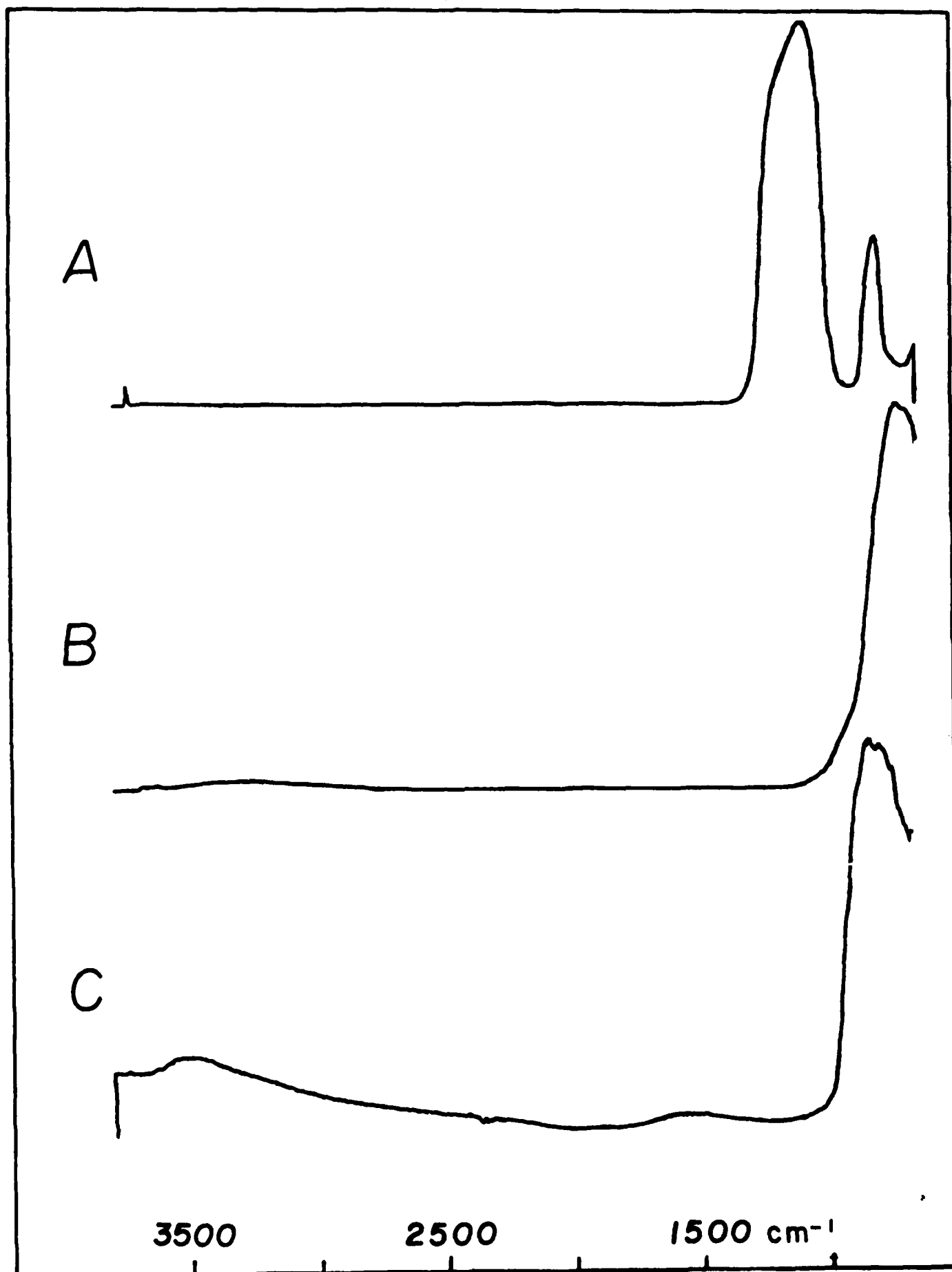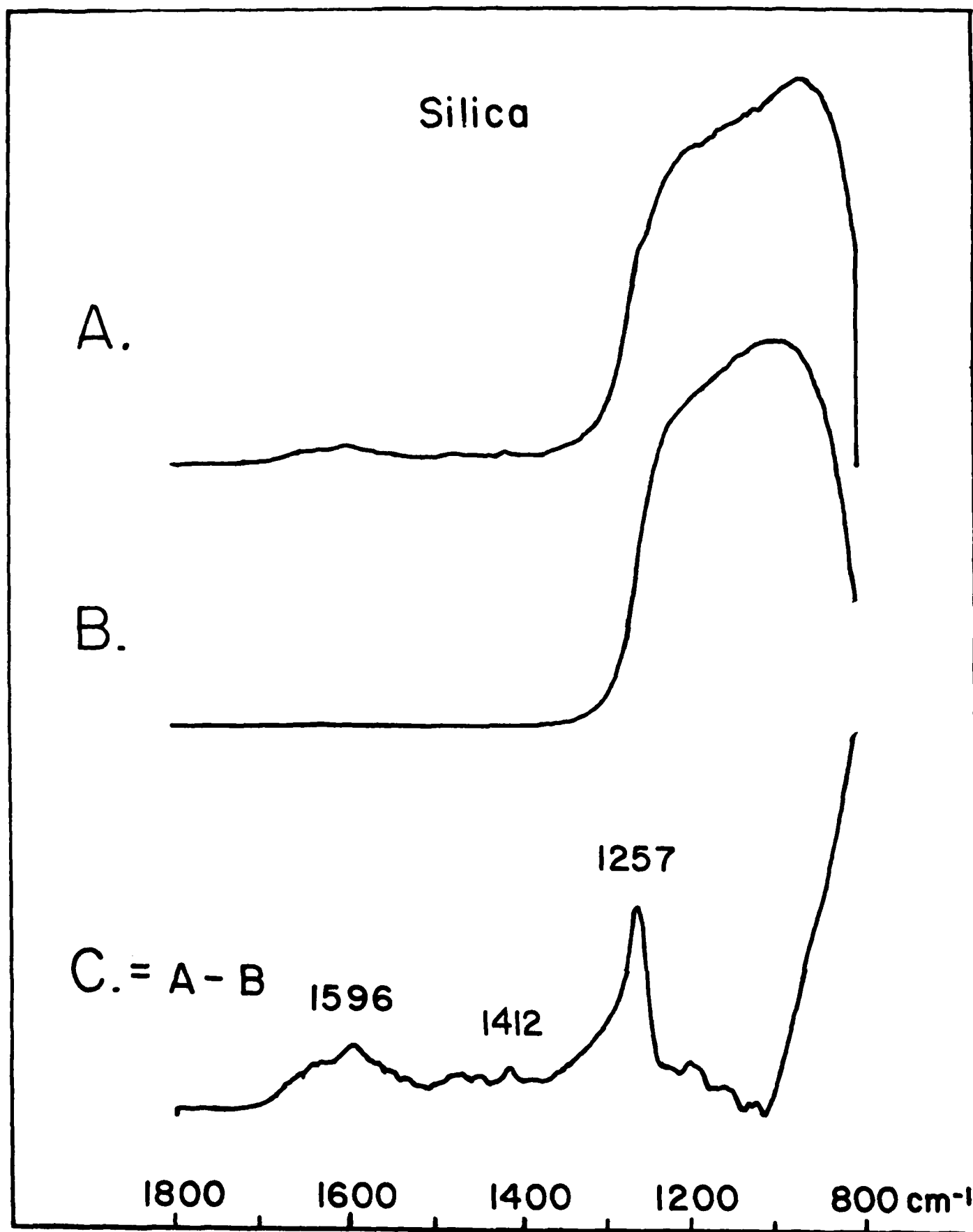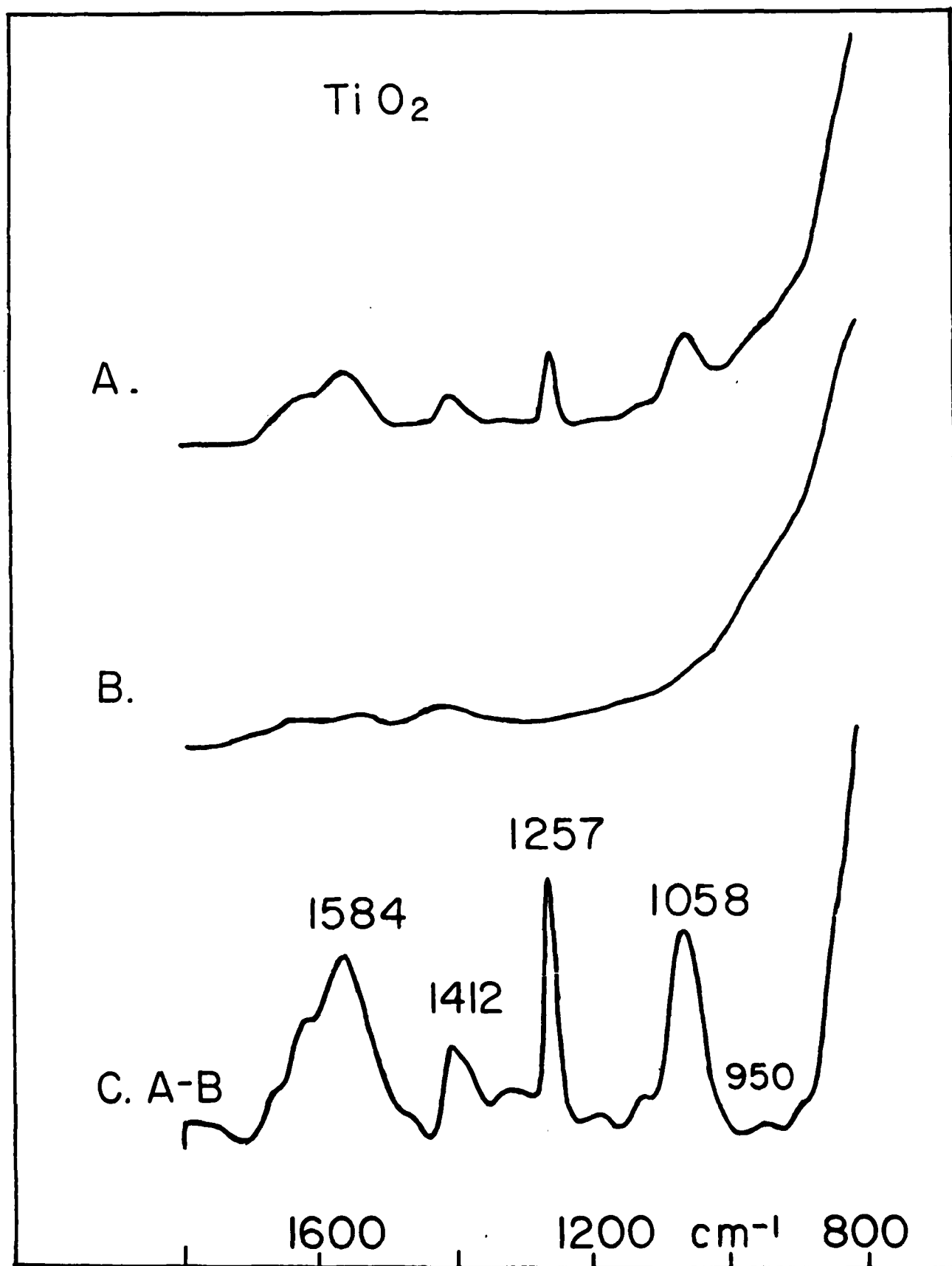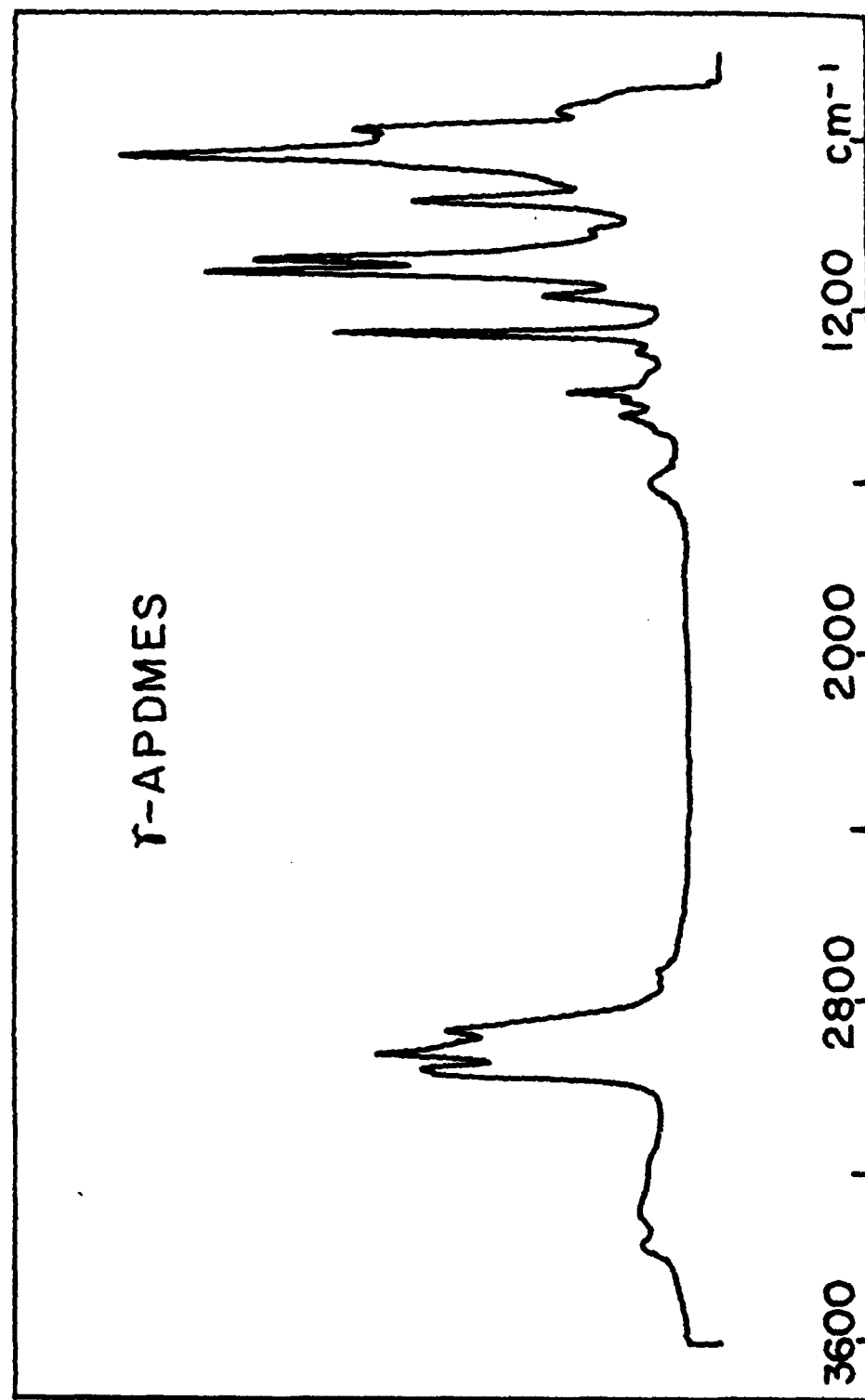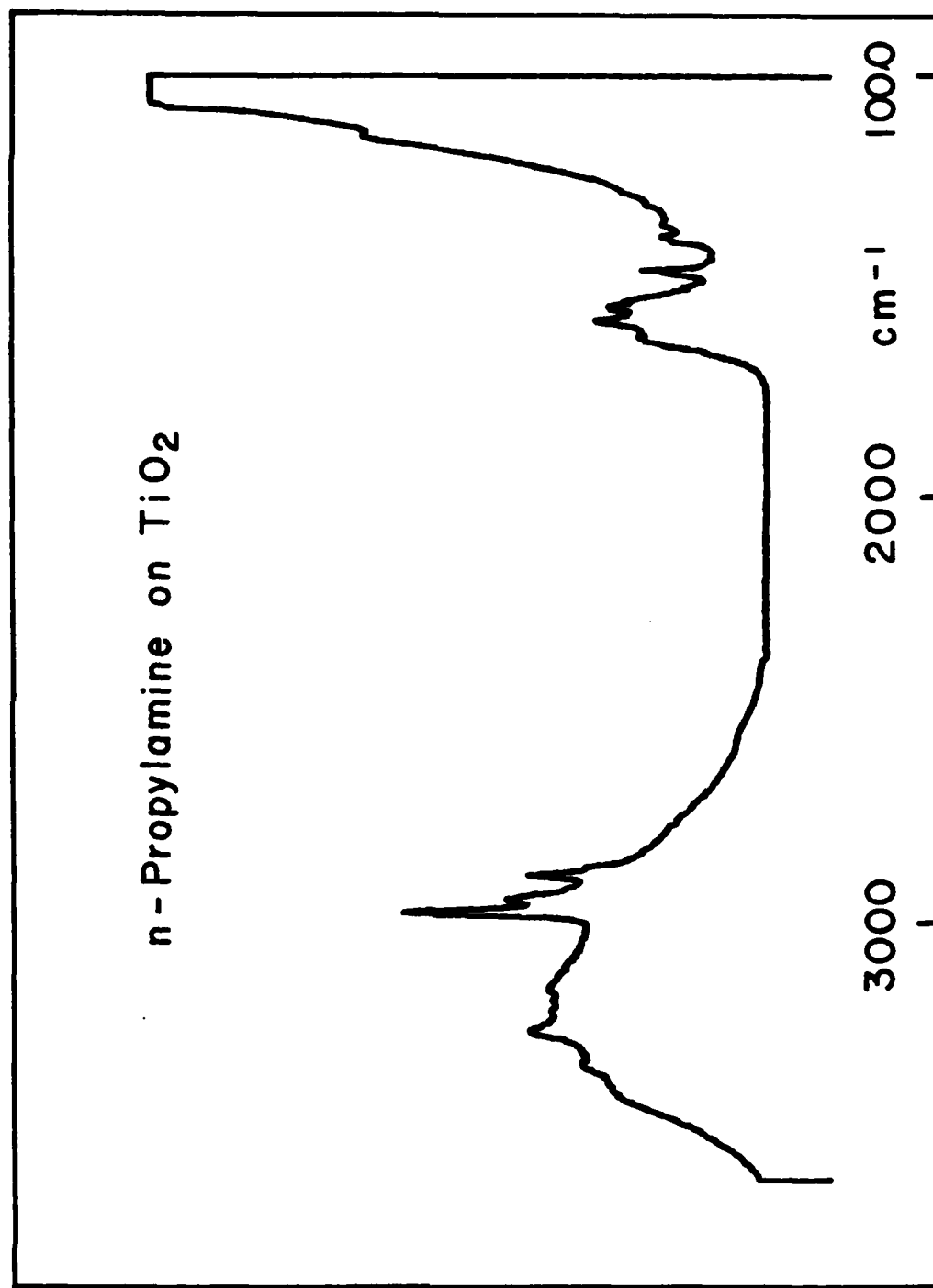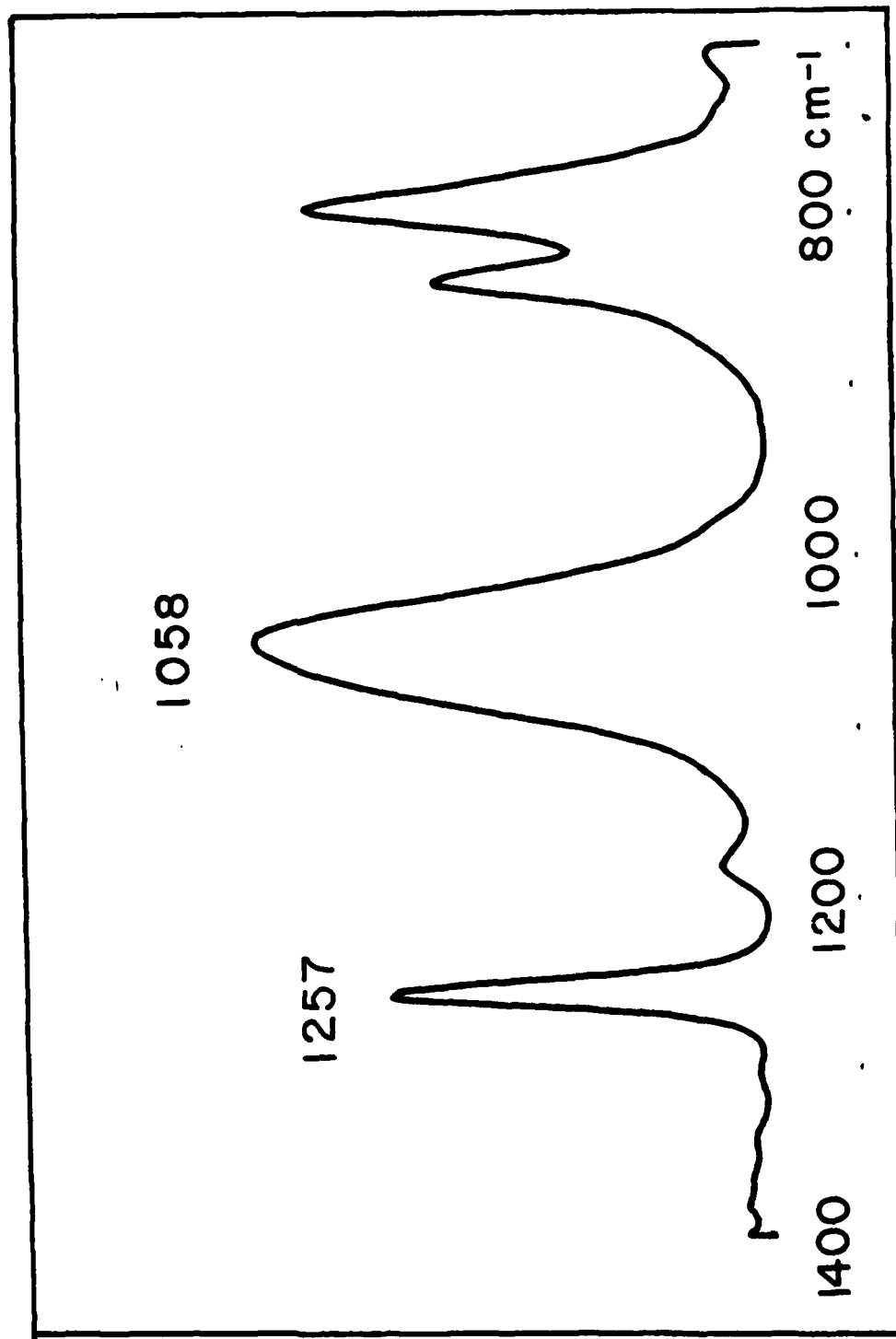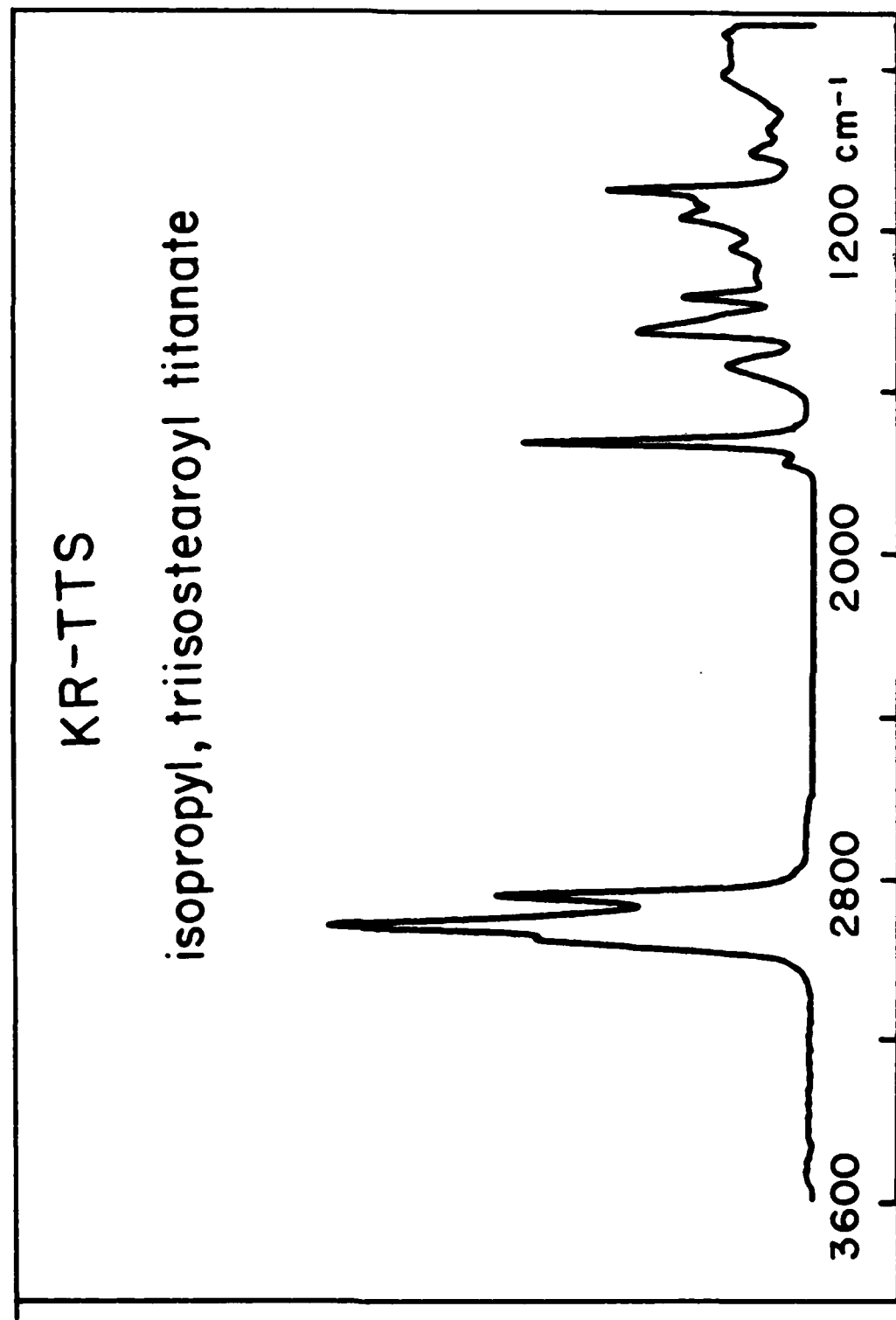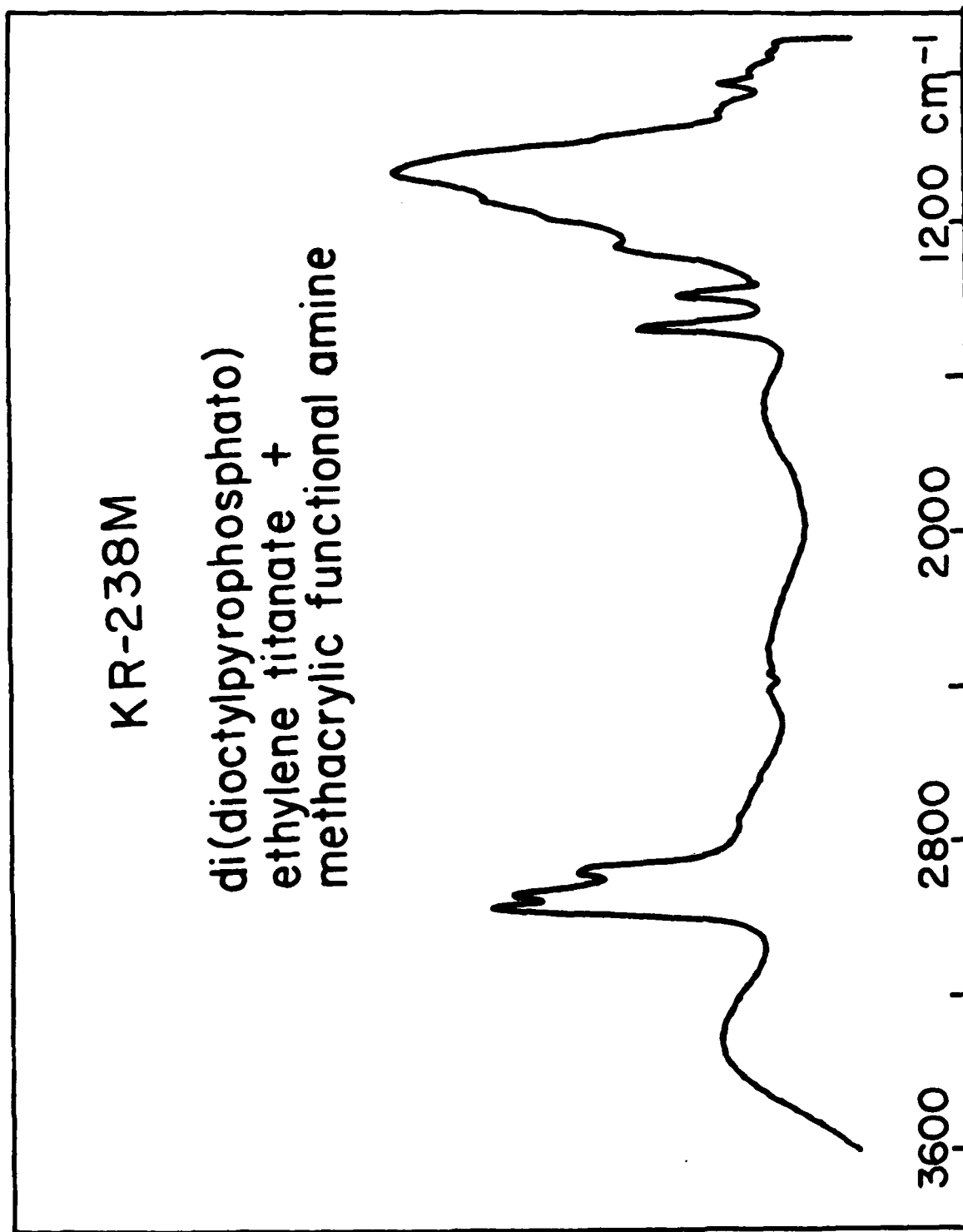
Figure 10

KR-TTS on Silica

Figure 11

Figure 12

Aluminum oxide

Figure 13

Figure 14

γ-APDMES on TiO$_2$

80°C

A. 3 days

B. 30 hrs

C. 6.5 hrs

D. 50 min

E. 10 min

1275

1400   1200   1000   800   cm^{-1}

APDMES

Area under 1257 cm⁻¹
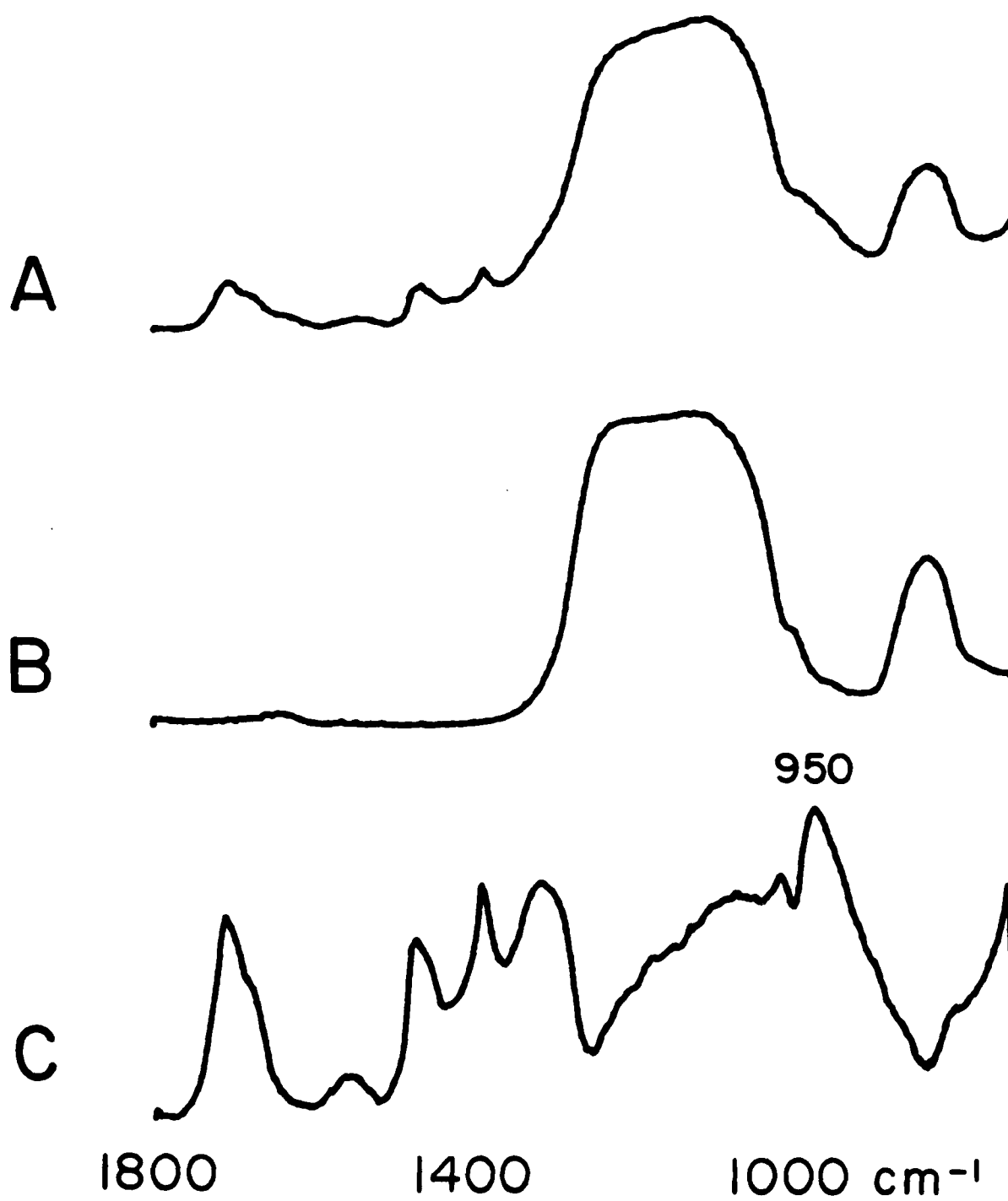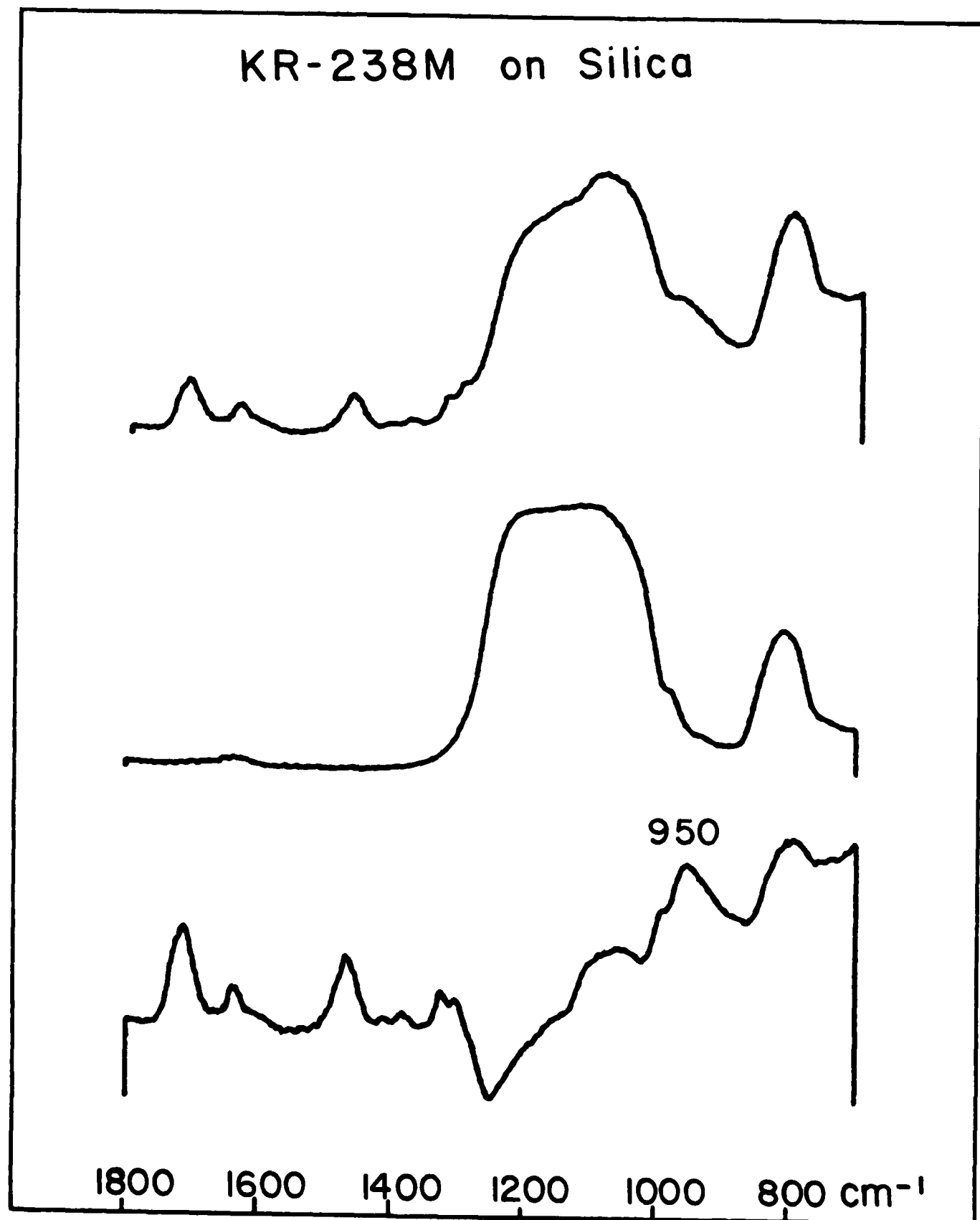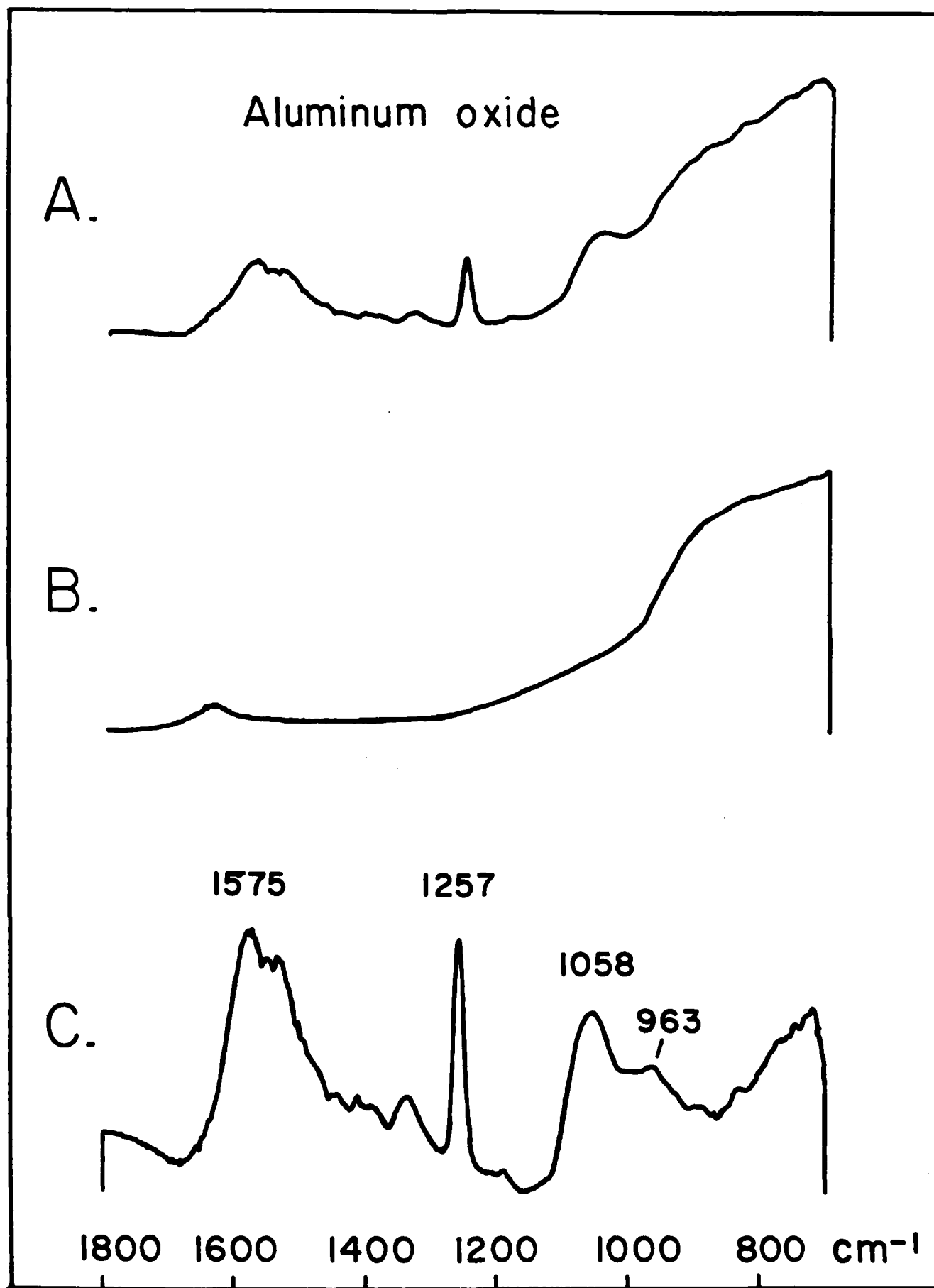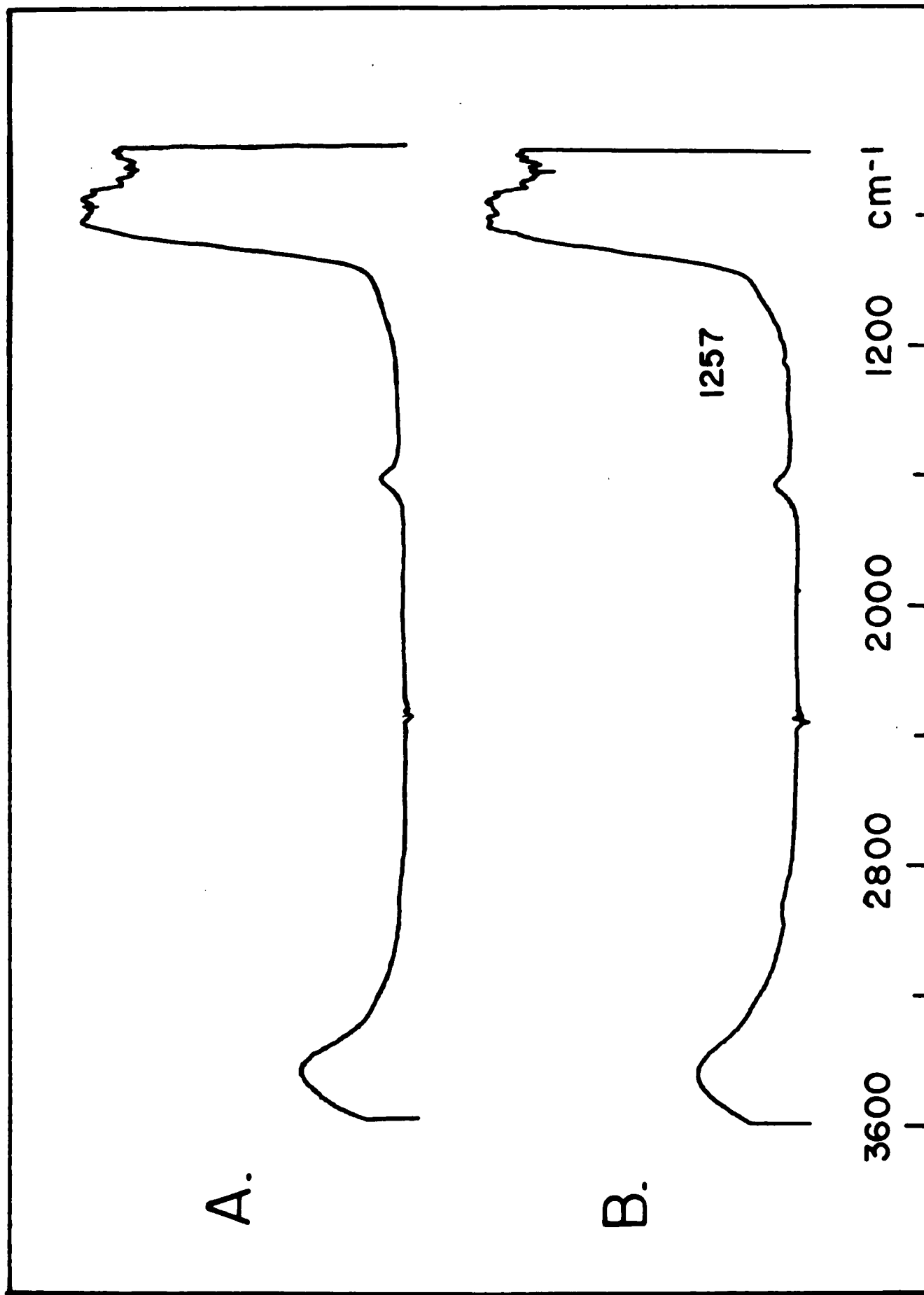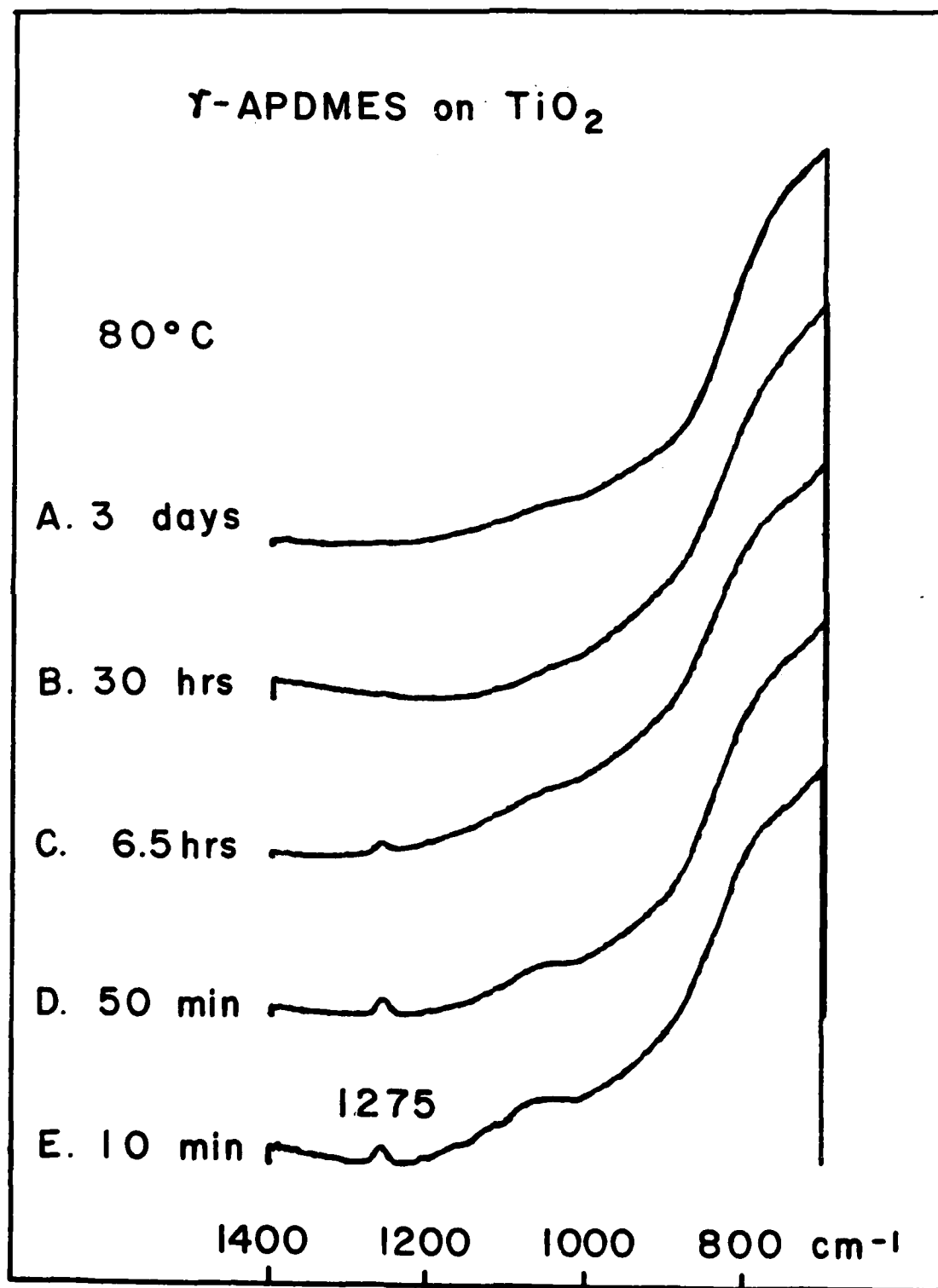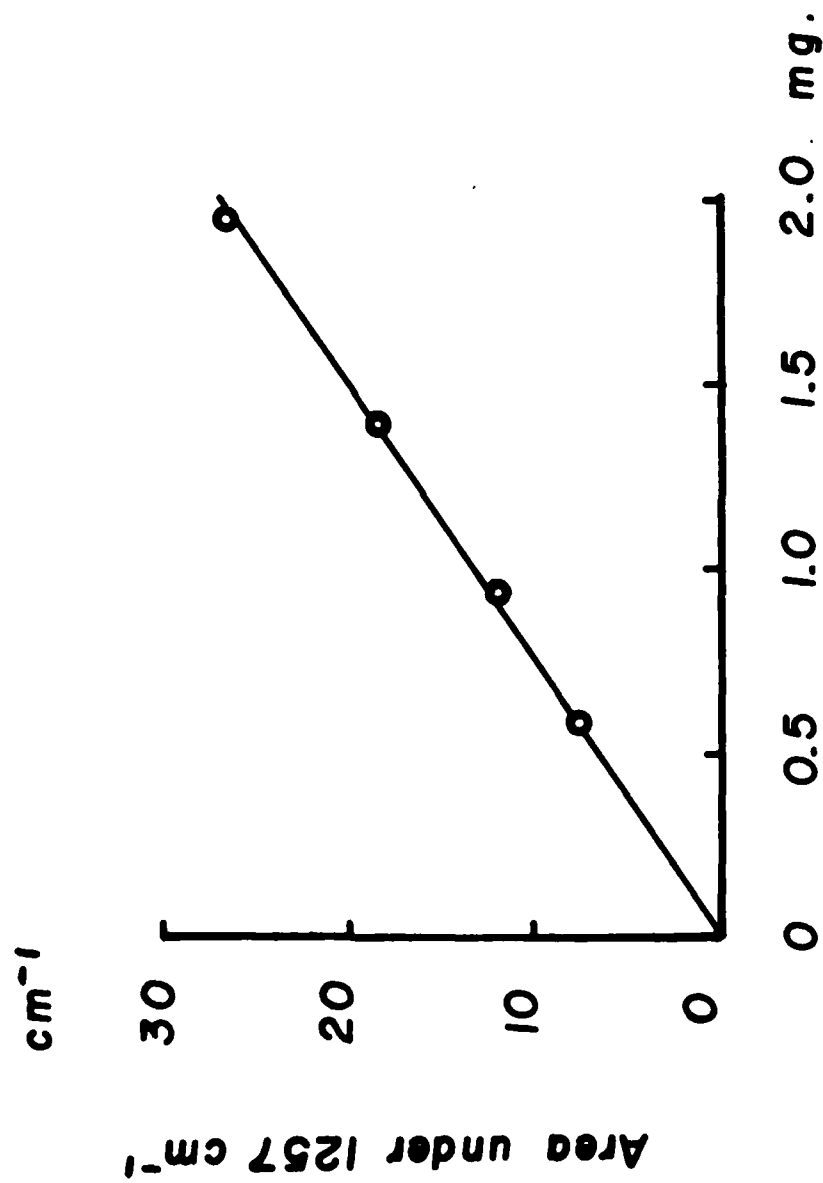
Figure 15

Calibration curve

Band at

Titanium oxide 690 cm⁻¹
Silica 1058 cm⁻¹
Aluminum ox. 830 cm⁻¹
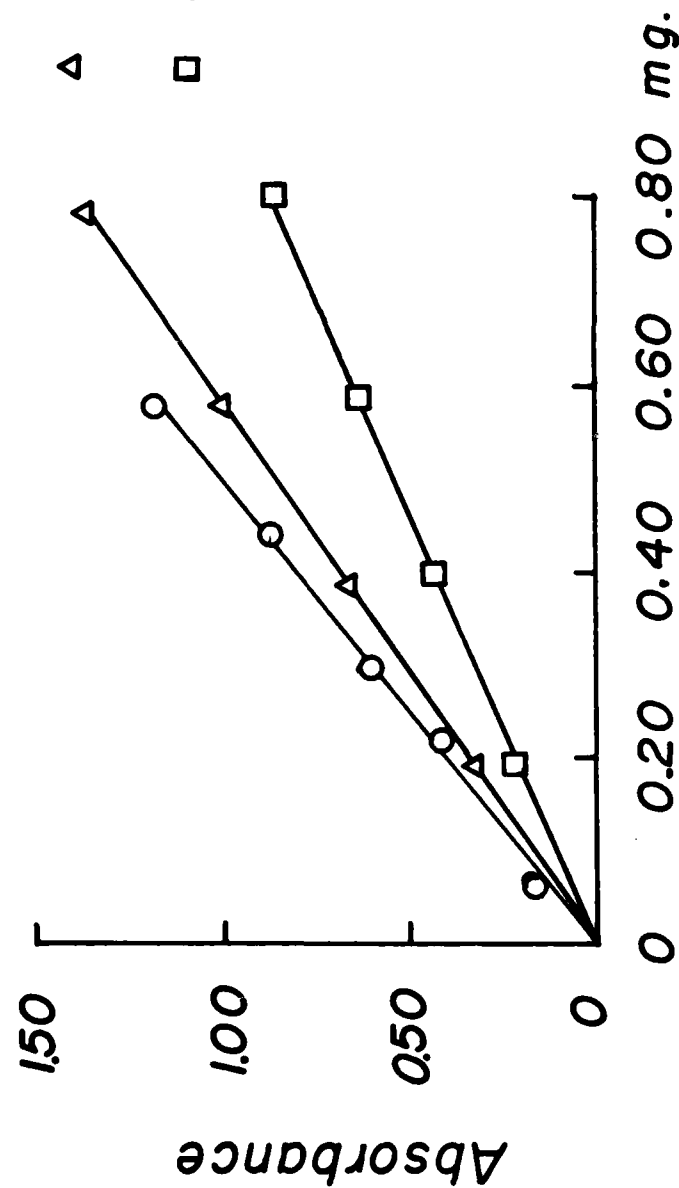
Figure 16

Figure 17

Figure 18

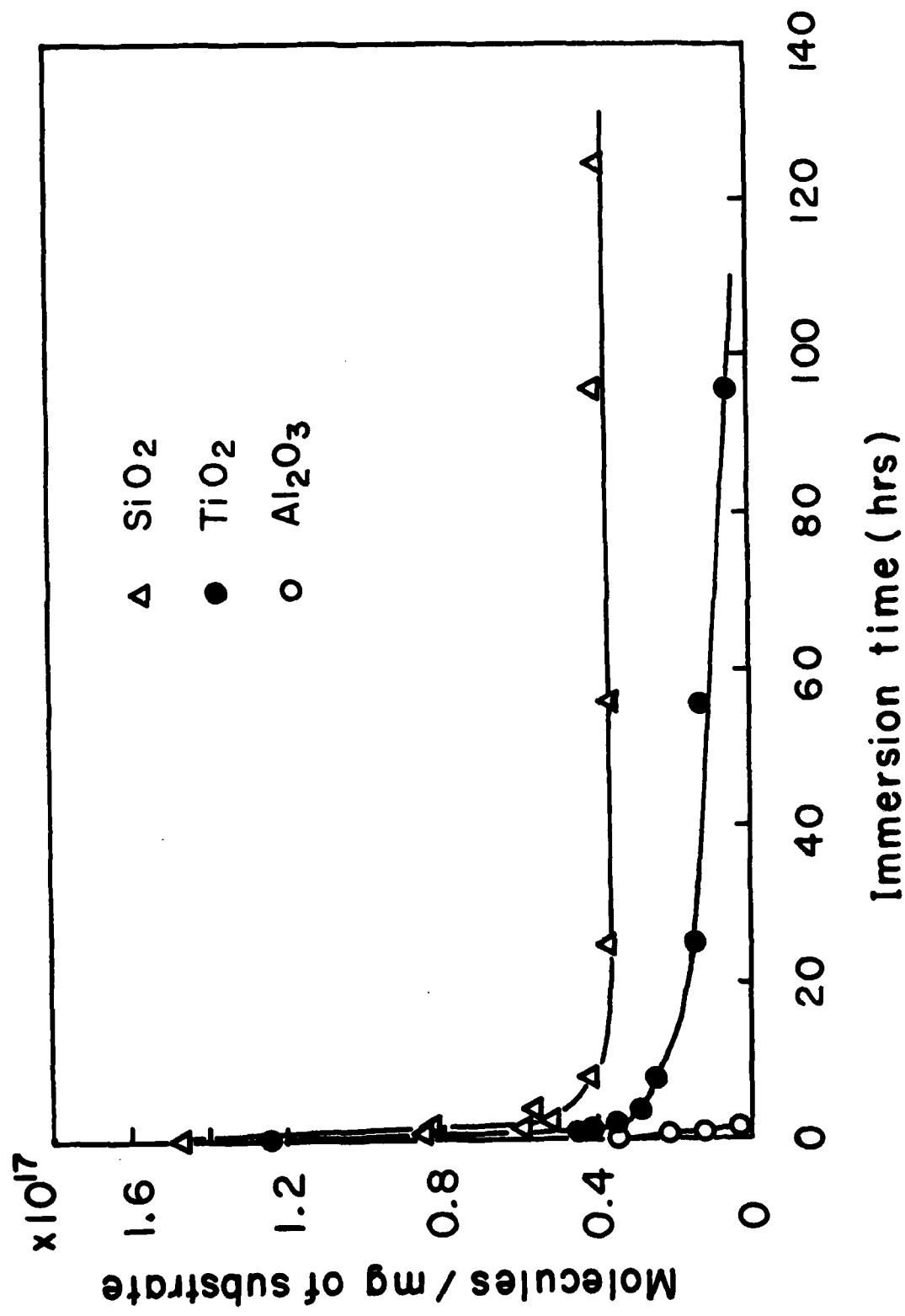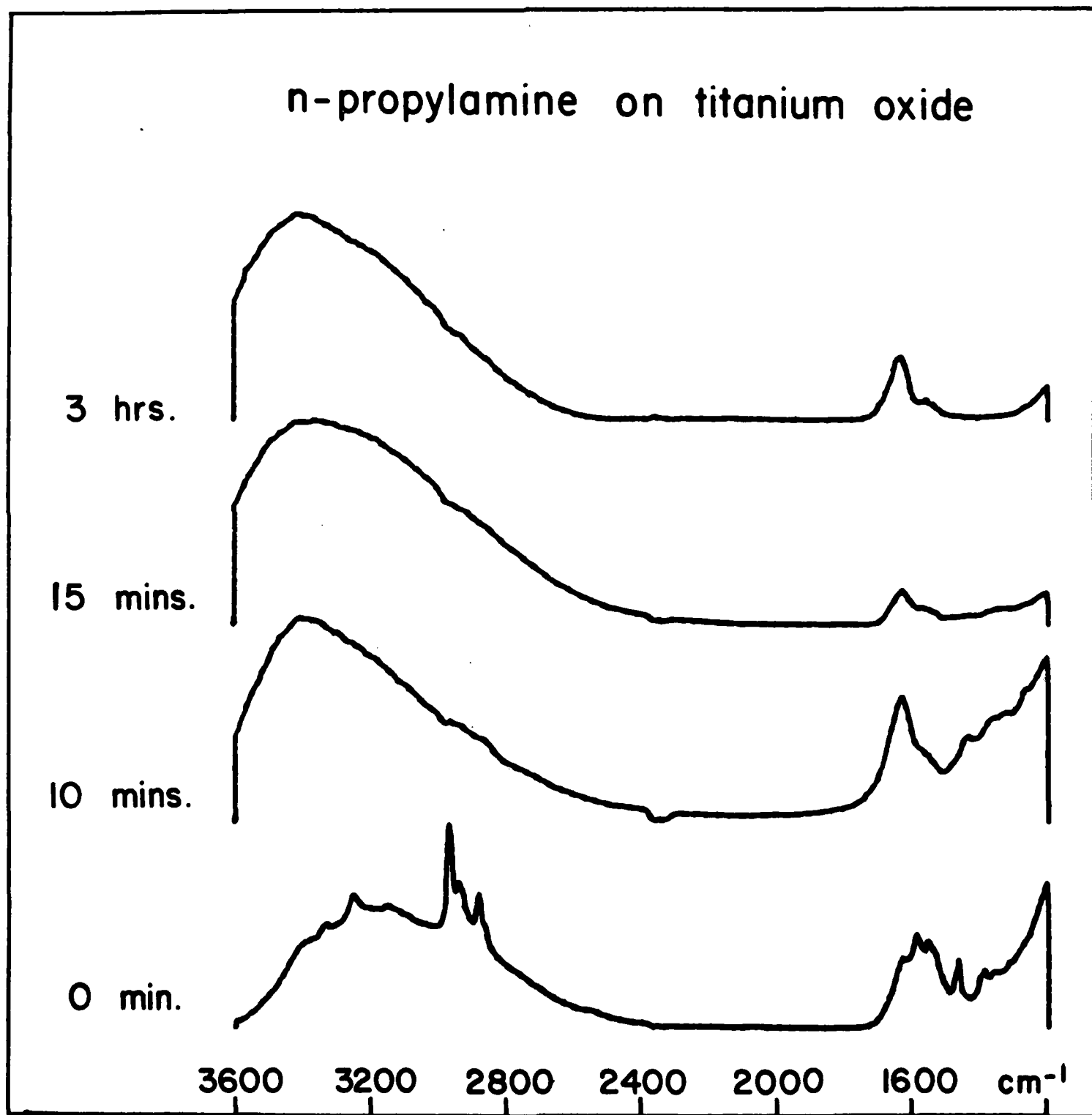Figure 19

n-propylamine on titanium oxide

3 hrs.

15 mins.

10 mins.

0 min.

3600   3200   2800   2400   2000   1600   cm⁻¹

END

FILMED

2-83

DTIC